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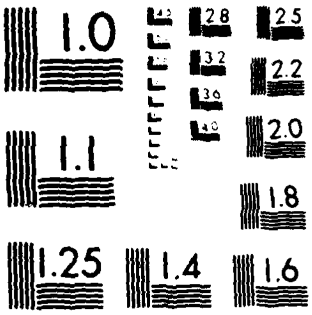

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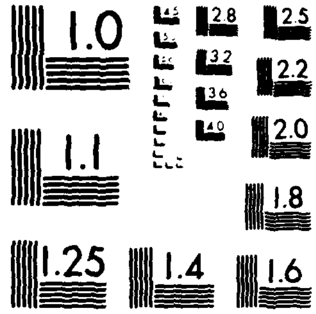

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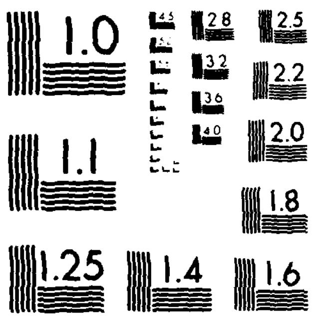

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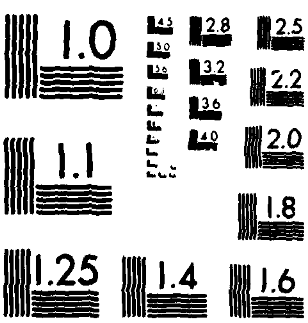

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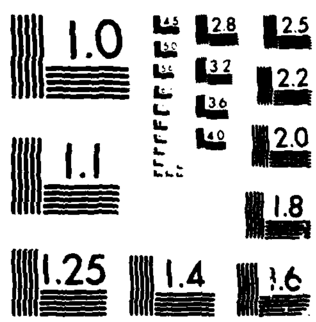

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FINAL REPORT

to the

Air Force Office of Scientific Research

for research on

Structure-Property Relationships in Intercalated Graphite

AFOSR Contract # F 49620-81-C-0006

for the years

October 1, 1980 - September 30, 1982

Principal Investigator: M.S. Dresselhaus

Co-Principal Investigator: G. Dresselhaus

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October 1, 1982

Table of Contents

1.0 Abstract

Under this contract a study has been carried out on the electronic ~~(§3.1)~~, lattice (~~§3.2~~), magnetic (~~§3.3~~), structural (~~§3.4~~), and thermal transport (~~§3.5~~) properties of intercalated graphite, including the modeling of these properties. The research program being carried out under this grant has been directed toward gaining an increased and fundamental understanding of the properties of graphite intercalation compounds in order to be able to produce better materials with more controlled physical properties.

By using diverse experimental techniques it is possible to correlate and interrelate the electronic, lattice, structural, magnetic and thermal transport properties of intercalated graphite and to interpret the dependence of these properties on the stage of the intercalation compound. During the two year period of this contract major advances have been made in each of these areas. Particularly noteworthy is the use of high resolution electron microscopy to monitor the c-axis and in-plane ordering on an atomic scale. Using single crystal Kish graphite host material, we have found evidence for large regions of defect-free single phase intercalant superlattices with dimensions of at least one order of magnitude greater than expected on the basis of previous work. A major advance has ~~also~~ been made in the use of high resolution x-ray scattering to study structural phase transitions in the graphite-bromine system, which is of fundamental interest to current theoretical work on phase transitions in two-dimensions. In addition new work on superconducting compounds has been initiated.

2.0 Personnel Involved with Research Program

M.S. Dresselhaus, Principal Investigator

G. Dresselhaus, Co-Principal Investigator

H. Mazurek, Postdoctoral (synthesis, characterization, structural studies) - left July 15, 1981

C. Nicolini, Postdoctoral (synthesis, characterization, magnetic studies, magnetoreflection experiment)

M. Shayegan, Graduate Student (thermal conductivity, specific heat at high magnetic fields, Shubnikov de-Haas studies of the Fermi surface)

M. Elahy, Graduate Student (magnetic susceptibility studies of magnetic properties)

A. Erbil, Graduate Student (Raman spectroscopy, high resolution x-ray scattering)

C.W. Lowe, Fellowship Graduate Student (infrared spectroscopy)

R. Al-Jishi, Graduate Student (modeling of phonon dispersion relations)

G. Timp, Graduate Student (electron microscopy, high field magneto-resistance, modeling)

L. Salamanca-Riba, Graduate Student (electron microscopy, magnetic properties)

E. Kunoff, Graduate Student (modeling of optical properties)

A. Kress, Undergraduate Student (synthesis)

M. Postman, Undergraduate Student (Raman spectroscopy)

Subcontract with Boston University

G.O. Zimmerman, Professor of Physics (magnetic properties)

S. Millman, Graduate Student (magnetic properties)

2.1 Invited Seminars

A list of invited senimars during the two year period of this contract is presented below. The principal investigator (MSD) was appointed the Graffin Lecturer of the American Carbon Society for 1982, and some of the seminars are in connection with the Graffin Lectureship.

March 1980, Invited Talk-American Physical Society, Phoenix (GD)

November 1980, Physics Colloquium, Boston University (GD)

November 1980, Industrial Sponsors Seminar, MIT (MSD)

January 1981, Physics Colloquium, University of Rhode Island (MSD)

February 1981, Seminar, Wright-Patterson Air Force Base (MSD)

March 1981, Seminar, Xerox, Palo Alto, Cal (MSD)

May 1981, Seminar, Xerox, Rochester, NY (MSD)

June 1981, Lax Symposium, MIT (MSD)

July 1981, Invited Talk, International Conference on the Physics of Intercalation, Trieste, Italy (GD)

October 22, 1981, Chemistry Division Seminar, Naval Research Laboratory, Washington, DC (MSD)

November 19, 1981, Laboratory-wide Colloquium, Shell Development Laboratory, Houston, Texas (MSD)

January 26, 1982, Physics Colloquium, University of Oregon, Eugene, Oregon (MSD)

January 27, 1982, Solid State Physics Colloquium, University of Washington, Seattle, WA (MSD)

February 10, 1982, Solid State Seminar, CCNY, New York (MSD)

February 18, 1982, Physics Colloquium, MIT (MSD)

February 23, 1982, Colloquium, Union Carbide Research Center, Parma, Ohio (MSD)

February 24, 1982, Physics Colloquium, Case-Western Reserve (MSD)

March 1, 1982, Francis Bitter National Magnet Laboratory Colloquium Series, MIT (MSD)

March 17, 1982, Physics Colloquium, University of Kentucky, Lexington, KY (MSD)

March 25, 1982, Laboratory Colloquium, Brookhaven National Laboratory (MSD)

March 29, 1982, Solid State Seminar, University of Kentucky, Lexington, KY (GD)

March 30, 1982, Solid State Seminar, Oak Ridge National Laboratory (GD)

March 30, 1982, Chez Pierre Seminar, MIT (MSD)

March 31, 1982, Physics Colloquium, University of Massachusetts (MSD)

April 14, 1982, Physics Colloquium, Wellesley College (MSD)

June 3, 1982, Program Review, Magnet Laboratory, MIT (MSD)

June 10, 1982, Solid State Division Seminar, Oak Ridge National Laboratory (MSD).

June 17, 1982, Technical Center Seminar, Celanese Corp., Summit, NJ (MSD)

July 8, 1982, Laboratory Seminar, General Atomic, San Diego, Cal (MSD)

September 29, 1982, Physics Colloquium, Boston University (MSD)

2.2 Conference Papers

The conference papers presented during the two year period of the contract are listed in §4.0, and include the following.

American Physical Society, March 1981, Phoenix

Invited Talk, "Electron and Phonon Dispersion Relations in Graphite Intercalation Compounds" (GD).

15th Biennial Carbon Conference, Philadelphia, June, 1981

Twelve papers listed in §4.0 as [5-16].

Physics of Intercalated Graphite, Trieste, Italy, July, 1981

Paper listed in §4.0 as [20].

Invited Talk, "Properties of Magnetic Graphite Intercalation Compounds", (GD).

American Physical Society, March 1982, Dallas

Four papers listed in §4.0 as [42-45].

2.3 Coupling Activities

The MIT group is strongly coupled to international activities on graphite intercalation compounds.

We collaborate on studies of the infrared, electronic and lattice properties of intercalated graphite with Professor P.C. Eklund and his group at the University of Kentucky; they have a strong experimental program and we work with them on the modeling and analysis of the resulting spectroscopic data. This collaboration has been in progress during the two year period of this contract. Paper 46 (see §4.0) resulted from this collaboration, and other papers are in preparation. During the last year the collaboration expanded to include Drs. Harold Smith and R. Nicklow of Oak Ridge National Laboratory to carry out neutron scattering experiments on graphite-$SbCl_5$ compounds.

The collaboration with Professor Zimmerman at Boston University continued on the susceptibility studies of magnetic intercalation compounds. Starting November 1, 1981, this group has been receiving subcontract funding for their part of the collaborative effort. Papers 19, 20, 31 (see §4.0) resulted from this collaboration.

A collaborative effort with Drs. L. Passell and J. Axe of Brookhaven National Laboratory on neutron scattering in intercalated graphite has been in progress. The focus of this work has been both on phonon dispersion relations and on the identification of the magnetic spin ordering associated with the magnetic phase transitions in the graphite-$FeCl_3$ system. In this collaboration, we prepared and characterized the samples, they made the neutron scattering measurements, and we did most of the modeling. Papers 11 and 25 listed in §4.0 resulted from the work on the phonon dispersion relations. The work on the magnetic spin ordering is continuing through collaboration with Prof. R.J. Birgeneau of MIT who has been doing neutron scattering experiments at Brookhaven on the graphite-$CoCl_2$ system.

X-ray measurements of the effect of intercalation on the lattice constants of graphite have been carried out in collaboration with Professor R. Ogilvie of the Department of Materials Science and Engineering, MIT (paper 36 in §4.0). Professor B.J. Wuensch of the Department of Materials Science and Engineering, MIT has provided significant help with the interpretation of x-ray data. During the second year of this program, high resolution x-ray scattering experiments on the graphite-Br_2 system were undertaken in collaboration with Professor R.J. Birgeneau of the Department of Physics, MIT to study the phase transition from a commensurate intercalate ordering to a striped phase incommensurate ordering. This high resolution study also addresses the observation of two-dimensional melting in the bromine layer.

With regard to our electron microscopy studies, Professor Linn Hobbs of the Department of Materials Science and Engineering, MIT has been especially helpful (paper 46 in §4.0). With regard to our low temperature experiments (below 1 K), the expertise and instrumentation provided by Dr. P. Tedrow of the Francis Bitter National Laboratory has been envaluable (paper 33 in §4.0).

2.4 New Discoveries, Patents or Inventions

None.

3.0 Progress Report

We present below a brief summary of accomplishments during the two year period of this contract on the "Structure-Properties Relationships in Intercalated Graphite".

3.1 Electronic Properties

3.1.1 Studies of the Shubnikov-de Haas Effect in Intercalated Graphite

A study of the Fermi surface of alkali metal graphite intercalation compounds (GIC) has been carried out using the Shubnikov-de Haas effect (papers 10, 29 in §4.0) demonstrating the stage dependence of the Fermi surface and the relation of the Fermi surface of intercalated graphite to that in pristine graphite. A discussion of effective mass measurements by a variety of experimental techniques has been presented (paper 26). Work is in progress on the study of the Fermi surface of the potassium-amalgam GIC which are of interest as superconducting materials. Also under investigation is the Fermi surface of the $CoCl_2$ GIC system with particular relevance to changes in the Fermi surface associated with the magnetic phase transition in the vicinity of 9.5 K.

3.1.2 Magnetoreflection Studies

A review of magnetoreflection results on various graphite intercalation compounds has been presented. The major conclusions of the magnetoreflection studies are that the electronic structure of GIC can be related to that of pristine graphite, and that the Slonczewski-Weiss-McClure Model for graphite can be applied with proper modification to intercalated graphite (paper 8).

These conclusions are shown to be compatible with the Fermi surface measurements on these compounds (papers 4 and 5), and to have implications on their transport properties.

Using the same equipment as was used for the magnetoreflection studies of intercalated graphite, we carried out the first magnetoreflection study on a doped semimetal, tin-doped bismuth (paper 35), showing that the basic rigid band model is applicable, though with some modification of band parameters. The magnetoreflection spectra show additional Landau level transitions caused by the symmetry-breaking impurities.

3.1.3 Modeling the Electronic Energy Band Structure of Intercalated Graphite

A model for the electronic energy band structure for intercalated graphite has been developed, the formalism depending on symmetry considerations such as k_z-axis zone folding to account for the staging phenomenon, characteristic of intercalated graphite. The advantage of this model is its general applicability to any intercalant and to any stage. Furthermore, a similar formalism can be used to obtain dispersion relations for phonons and for Landau levels, and we have also made these extensions of the formalism. From a computational point of view, the computer programs developed for the electronic problem have proven useful for detailed calculations for the phonons and for the Landau levels.

The calculations of the electronic structure are now completed and described in papers 2, 3, 7, 30 and in the invited talk, paper 22 in §4.0. The extension of these techniques to the calculation of the Landau levels is given in papers 8 and 13.

An application of the calculations on the electronic structure to an explanation of the optical properties of GIC is in progress. Measurements of the frequency-dependent reflectivity for various stages of the $CoCl_2$ GIC system is nearing completion (paper 43) and a calculation of the frequency-dependent dielectric constant based on the calculated dispersion relations E(k) is in progress.

3.2 Phonon Studies

3.2.1 Raman Spectroscopy of Intercalated Graphite

Structural phase transitions in the graphite-bromine system have been studied by A. Erbil through observation of anomalies in the temperature dependence of the intensity, linewidth and lineshape of the Raman spectra of the intercalant. This is the first time that such types of structural phase transitions have been observed through lattice mode studies of intercalated graphite (papers 16, 27). High resolution x-ray scattering experiments are now in progress in collaboration with Prof. R.J. Birgeneau and his group to identify in detail the nature of these structural phase transitions. In this work we have made the most convincing observation to date of a transition to an incommensurate striped domain phase structure. This work is continuing and is being further augmented by high resolution electron microscopy studies by G. Timp on the graphite-Br_2 system.

Recently the Raman scattering technique has been applied to the observation of strong zone-folded modes in the stage 1 potassium-amalgam GIC (paper 48). Depending on the method of sample preparation, several in-plane intercalant orderings can occur in this system, including the ($\sqrt{3} \times \sqrt{3}$) R30°, (2 x 2) R0° and ($\sqrt{3}$ x 2) R(30°,0°) orderings. The observed zone-folded Raman spectra are consistent with these in-plane structures which are observed directly by transmission electron microscopy in similarly prepared samples.

3.2.2 Inelastic Neutron Scattering Studies of Intercalated Graphite

Through our collaborative program with a group at Brookhaven National Laboratory, inelastic neutron scattering measurements have been made to obtain the low frequency longitudinal phonon dispersion relations for the graphite-$FeCl_3$ system (papers 11 and 25). In this collaboration, the samples were prepared and characterized at MIT, the neutron work was done at Brookhaven and the modeling of the phonon dispersion relations was carried out at MIT. We are also actively engaged in a collaborative study of phonon dispersion relations with Professor P.C. Eklund and the inelastic neutron scattering group at Oak Ridge National Laboratory to study phonon dispersion relations in the graphite-$SbCl_5$ system. This work is continuing.

3.2.3 Modeling of Phonon Modes in Intercalated Graphite

The phonon dispersion relations for intercalated graphite have been calculated on the basis of a model similar to that for the electronic dispersion relations, and these calculations in generalized form are presented in papers 15 and 41. In order to obtain quantitative agreement with the pertinent experimental data, it was necessary to carry out a more precise calculation of the phonon dispersion relations for pristine graphite (papers 21 and 34).

The phonon modeling work for the intercalation compounds has largely focused on the application of the results of the low frequency phonon branches measured by inelastic neutron scattering to the calculation of 3-dimensional phonon dispersion relations. These calculations have now been completed for the alkali metal donor compounds and are in progress for a few typical acceptor compounds.

In collaboration with P. Lespade, we have calculated the Raman spectra for disordered graphite with particular reference to characterizing the graphitization process as a function of the heat treatment temperature of the carbon material. In this work, the calculations for graphite (described above) were extended to 2-dimensional crystallites of varying mean sizes (paper 38).

3.2.4 Deformation Potential and Magnetostriction

The relationship between lattice strain and intercalation suggested by our Raman studies has developed into an experimental and theoretical program on the relation between strain and the electronic structure of graphite. Magnetostriction experiments have been carried out on both graphite and graphite intercalation compounds, and are described in papers 17 and 24, and a discussion of the form of the deformation potential in graphite is presented in paper 14.

3.3 Magnetic Properties of Graphite Intercalation Compounds

3.3.1 Magnetic Susceptibility Studies

Magnetic intercalation compounds are prepared by selection of intercalants which are themselves magnetic. The great advantage of the intercalated graphite system for studying magnetic interactions is that by increasing the stage index, the separation between magnetic layers can be increased, thereby controlling the magnitude of the magnetic interlayer interaction. Magnetic phase transitions in these systems are most sensitively measured by the magnetic susceptibility technique.

Magnetic susceptibility measurements have therefore been carried out on a series of $FeCl_3$ compounds for stages 1, 2, 4 and 6 and for several $CoCl_2$ and $NiCl_2$ compounds (papers 19, 31). The similar behavior observed for the different magnetic intercalants and stages indicated the need for precise absolute measurements. The need to determine the functional dependence of χ on temperature and magnetic field for theoretical modeling considerations also indicated the need for more precise measurement capabilities. For this reason, much effort has been devoted to improved instrumentation in the ac susceptibility bridge apparatus. This instrumentation is now complete, and precise determination of the temperature dependence of the susceptibility has been carried out for stage 3 and 5 $CoCl_2$ intercalation compounds.

Measurements are now in progress for other compounds. The experimental program has been directed to precise measurement of the magnetic field dependence of the susceptibility. The measurements will be interpreted in terms of existing two and three-dimensional models for the susceptibility. Because of the finite size of the magnetic domains in these samples, the current theroetical models will have to be extended to be applicable to the experimental measurements on GIC.

3.3.2 Magnetic Heat Capacity Studies

In connection with the unusual magnetic phases studied with the susceptibility technique, heat capacity measurements have also been undertaken to study the magnetic phase transitions. Of particular interest in our work are measurements of the magnetic field dependent heat capacity to allow us to explore the magnetic phases in detail. To carry out these measurements making extensive use of an on-line computer, a cryostat was specifically designed and built by Shayegan for the magnetic field-dependent heat capacity measurements. This system is now finished and successful measurements have been made on several $CoCl_2$ compounds in fields up to 14 T, revealing a broad (width of about 5 K) anomaly at about 9 K and associated with the magnetic phase transition. The observed anomaly is most intense in the zero field heat capacity data and is largely suppressed in fields above about 3 T. This enables a separation to be made between the magnetic, electronic and lattice contributions to the heat capacity. The entropy change associated with the magnetic ordering has been measured and found to be much less than that associated with a 3-dimensional phase transition, in agreement with Monte Carlo calculations based on 2-dimensional models.

3.3.3 Fermi Surface Measurements

To determine the electronic contribution to the heat capacity, Shubnikov-de Haas measurements of the Fermi surface have been initiated on the same compounds as are being studied in the magnetic heat capacity measurements to find the carrier densities and carrier masses associated with each of the carrier types. Particular attention will also be given to the investigation of possible changes in the Fermi surface at the magnetic phase transition. By determining the Dingle temperature above and below the magnetic transition temperature T_c, we will also attempt to look for possible changes in scattering processes at T_c.

3.4 Structural Properties

3.4.1 Multiphase Structure of Alkali-Metal GIC

Previous transmission electron microscopy studies in our group on alkali metal intercalated graphite provided strong evidence for a multiphase intercalant layer structure for stages $n \geq 2$. These observations have been confirmed by high resolution STEM (scanning transmission electron microscope) measurements on similar samples based on HOPG host materials (papers 12, 32). The STEM experiment has enabled us to look in detail into the multiphase intercalant regions using both real space imaging to "see" the islands and x-ray fluorescence measurements to map the intercalate density across the sample. The correlation between the real space imaging and x-ray fluorescence results shows island regions corresponding to higher intercalate densities than the background regions.

3.4.2 Lattice Fringe Studies on Intercalated Graphite

As a result of the delivery to M.I.T. of a new high resolution electron microscope, we have developed the capability to carry out lattice imaging measurements on graphite intercalation compounds. Our measurements have been carried out on intercalated samples prepared from single crystal kish graphite host materials. The results we have obtained are spectacular and are attracting a great deal of attention. The most unexpected result is that we have been able to observe (for the first time) large (100 Å x 2000 Å) defect-free regions in a well staged intercalation compound (stage 2 graphite-$SbCl_5$). The samples were grown by Prof. Peter Eklund of the University of Kentucky and the microscopy work was done by G. Timp. The results have important implications on the intercalation process and show that if Herold-Daumas domain walls are formed by intercalation, they must be separated by at least 2000 Å, an order of magnitude greater than had been thought to be the case from indirect inferences (paper 46).

3.4.3 Phase Transition to a Low Temperature Glassy Phase

A novel phase transition has been observed for the intercalate layers in stage 2 graphite-$SbCl_5$ from a commensurate $(\sqrt{7} \times \sqrt{7})R19.1°$ phase at room temperature to a glassy phase as the sample temperature is lowered below about 185 K. The phase transition exhibits hysteresis and has also been observed in the transport properties of this compound by Clarke and his co-workers. The samples for this work were prepared by Prof. Peter Eklund of the U. of Kentucky and all the electron microscopy measurements and analysis were carried out at MIT. We have also observed similar phase transitions in stage 1 and in higher stage compounds of the graphite-$SbCl_5$-system, though the transition temperature is stage dependent. Work is in progress to determine the stage dependence of these phenomena quantitatively.

3.4.4 Structural Studies of Potassium-Amalgam GIC

By use of kish single crystal host materials and high resolution transmission electron microscopy, a number of new phenomena associated with intercalate ordering have been observed. Results have been obtained with well-staged compounds for stages 1, 2 and 3. In the case of the stage 3 compound, we have achieved the first synthesis of this important compound which has been of great interest for the study of two-dimensional superconductivity.

One important achievement has been the direct observation of staging in this class of compounds by the lattice fringing method. Using electron diffraction we have identified three commensurate in-plane orderings in the stage 1 compounds: (2 x 2)R0°, ($\sqrt{3}$ x $\sqrt{3}$) R30°, and ($\sqrt{3}$ x $\sqrt{2}$) R(30°,0°) (see paper 42). Supporting evidence for these in-plane ordering assignments has been obtained by our observation of a number of Raman lines in the first- and second-order spectra (paper 48) attributed to in-plane zone-folding associated with these superlattice periodicities. The type of commensurate orderings in the stage 1 compounds is contingent on the preparation conditions, and different intercalate stoichiometries result in different in-plane orderings. No temperature dependent structural phase transitions are observed in electron diffraction over the temperature range $10 < T < 750$ K.

For the stage 1 potassium-amalgam GIC, in-plane lattice fringe images of $(10\bar{1}0)$ planes corresponding to both ($\sqrt{3}$ x $\sqrt{3}$)R30° and (2 x 2)R° in-plane superlattices have been studied. Of great interest are the large regions (~1000 x 1000 Å) of defect-free superlattice structures observed for both of these in-plane orderings.

3.4.5 Novel Phase Transitions in Bromine-Intercalated Graphite

High resolution x-ray scattering studies of stage 4 graphite-bromine have been carried out in collaboration with Professor Birgeneau and his group at MIT. For the stage 4 compound, the interlayer separation is sufficiently large (~ 17 Å), so that the interlayer intercalate interaction is weak compared with the graphite-bromine interlayer interaction, which is strong. The high resolution x-ray scattering results show a structural phase transition at 342.2 K from a commensurate phase with an in-plane ($\sqrt{3}$ x 7) superlattice structure to a striped domain phase occurring only in the 7-fold direction. The ($\sqrt{3}$ x 7) commensurate superlattice has been observed directly in selected area electron diffraction measurements carried out by G. Timp with the high resolution 200 CX JEOL transmission electron microscope.

The functional form of the commensurability follows a power law with exponent 1/2, in agreement with theoretical predictions. The relative displacements of successive harmonics in the Bragg peaks above the transition temperature are accurately predicted by a sharp domain wall model with $4\pi/7$ phase shifts. At higher temperatures (373 K), a two-dimensional melting transition occurs and is under investigation using the high resolution x-ray scattering technique. Also of significance with regard to models for the intercalation process, are the large in-plane coherence distances measured for the Br_2 intercalant, which exceeds 10,000 Å in both commensurate and incommensurate phases.

3.4.6 Temperature Dependence of C-Axis Interplanar Separations

The temperature dependence of the (00ℓ) x-ray reflections in graphite-$FeCl_3$ has been measured (paper 39). The c-axis unit cell, I_c, shows a large expansion with increasing temperature, associated with a large relative expansion of the Fe-Cl interplanar distances and a smaller expansion of the graphite-intercalant interplanar distances. The magnitude of the temperature coefficient of expansion of the Fe-Cl interlayer distance in the stage 1 graphite-$FeCl_3$ compound is in good agreement with that of pristine $FeCl_3$.

3.4.7 Effect of Intercalation on the In-Plane Lattice Constant of Graphite

In a related study, the effect of intercalation on the in-plane lattice constant of graphite has been measured (paper 36). It is found that intercalation has a very small effect on this lattice constant (less than 2 parts in 10^3 in all cases). The effect is larger for donor compounds than for acceptor compounds, and is positive for donor compounds and negative for acceptc. compounds. These findings are consistent with the effect of intercalation on the frequency of the graphite Raman-active E_{2g2} mode.

3.5 Transport Properties

3.5.1 Electronic and Lattice Contributions to the Thermal Conductivity

The temperature dependence of the in-plane thermal conductivity of various donor and acceptor graphite intercalation compounds has been studied, with particular attention to the graphite-$FeCl_3$ system and dilute graphite-potassium compounds (papers 6, 18). Our measurements show that the in-plane thermal conductivity at room temperature is dominated by phonon contributions, but is typically smaller than that of pristine graphite by about an order of magnitude. At low temperatures, the in-plane thermal conductivity for intercalated graphite is dominated by electronic contributions and is larger than for pristine graphite. Analysis of the functional form of the temperature dependence of the lattice and electronic contributions has provided quantitative information about lattice defects which are introduced by intercalation and which scatter both electrons and phonons. Measurements of the c-axis thermal conductivity on a donor (stage-5 graphite-potassium) and an acceptor (stage-2 graphite-$FeCl_3$) show only lattice contributions over the entire temperature range ($2 < T < 300$ K) that was measured. Thus, at low temperature we have a situation where electron transport dominates the in-plane thermal conductivity, but phonons dominate the c-axis behavior.

3.5.2 High Field Thermal Conductivity of GIC

To separate the electronic from the lattice contribution, the thermal conductivity of graphite intercalation compounds has been measured in high magnetic fields on a dilute donor and a dilute acceptor compound (paper 37). Because of the large magnetoresistance of these compounds, the Wiedemann-Franz law implies that at sufficiently high fields the electronic contribution can be made very small. In the high field regime, the entire thermal conductivity is due to the lattice. In our study, the electronic and lattice contributions to the thermal conductivity were successfully separated over almost the entire temperature range $2 < T < 50$ K using magnetic fields up to 15 T.

3.5.3 Thermopower Studies

The temperature dependence of the in-plane thermopower for both donor and acceptor compounds has been measured (papers 9, 18, 23). The sign of the thermopower for donors is negative, and for acceptors is positive. At low temperatures, the magnitude of the thermopower increases linearly with temperature and then becomes approximately independent of temperature at higher temperatures. The temperature dependence of the thermopower shows little stage dependence. A model based on phonon drag phenomena has been developed by Sugihara to explain our observations.

3.5.4 Temperature Dependence of C-Axis Electrical Resistivity and Thermopower of GIC

Results of the temperature dependence of the c-axis electrical resistivity and thermopower of a stage 5 graphite-potassium donor compound and a stage 2 graphite-$FeCl_3$ compound have been obtained in the temperature range $2 < T < 300$ K (paper 47). Our results considered in conjunction with the work of others show a different qualitative behavior for low and high stage compounds, with a graphitic behavior dominant for dilute GIC and a metallic behavior dominant for low stage compounds.

3.5.5 High Field Magnetoresistance Studies of Graphite

Of all conducting materials, graphite is the material having the best understood electronic band structure. It was thus very surprising to observe a high field anomaly in the magnetoresistance above 22 T, when the last Landau level passes through the Fermi level at 7.3.T. To address this anomalous observation, we have investigated the magnetoresistance of pristine graphite at high magnetic field (up to 28.5 T) and for temperatures down to 0.48 K using the high steady fields provided by the new hybrid magnet at the Francis Bitter National Magnet Laboratory (paper 33). The strong temperature dependence of the critical field seems to preclude an interpretation of this phenomenon in terms of known one electron properties of graphite, and suggests the occurrence of some kind of electronic phase transition. One plausible interpretation is the charge density wave instability of one-dimensional Landau subbands, proposed by Yoshioka and Fukuyama. The detailed behavior of the magnetoresistance, however, remains to be discussed theoretically.

This study is being continued by G. Timp with help from Dr. P. Tedrow at the National Magnet Laboratory with regard to study of the angular dependence of the high field anomaly. Timp has also carried out a calculation of the high field magnetoresistance expected from one-electron behavior with particular reference to the anomalous field dependence of the lowest quantum number Landau levels at the H point. A preliminary report of this work was given at the March 1982 meeting of the American Physical Society in Dallas (paper 45).

3.6 Preparation of Review Articles

Work is continuing on an article on the Optical Properties of Graphite Intercalation Compounds, in preparation for the Physics and Chemistry of Carbon Series (ed. P. Thrower). We hope to complete this manuscript during the calendar year 1983.

A review article on intercalated graphite for the Encyclopedia of Materials Science and Engineering has been completed and submitted for publication.

Another large review article on recent advances in intercalated graphite for the Physics and Chemistry of Solids series is in progress and a first draft of the manuscript has been completed. Revisions to the first draft are now being made and we expect to complete this manuscript during the Fall of 1982.

4.0 Publications

The following papers have either been accepted for publication or have come out during the 2 year period of this contract.

1. "Intercalation Compounds of Graphite," M. S. Dresselhaus and G. Dresselhaus, Advances in Physics, 30, 139 1981.

2. "Phenomenological Electronic Energy Bands in Graphite Intercalation Compounds," G. Dresselhaus and S.Y. Leung, Solid State Commun. 35, 819 (1980).

3. "Electronic Structure of Graphite-Alkali Metal Compounds," G. Dresselhaus, S.Y. Leung, M. Shayegan and T.C. Chieu, Synthetic Metals 2, 321 (1980).

4. "The Interrelation of Shubnikov-de Haas, Magnetoreflection, and Transport Properties of Alkali Metal Donor Intercalation Compounds," M.S. Dresselhaus, G. Dresselhaus, M. Shayegan and T.C. Chieu, Proceedings of the Fifteenth International Conference on the Physics of Semiconductors, Kyoto, 1980, J. Phys. Soc. Japan 49, Supplement A, 911 (1980).

5. "Magnetoreflection and Shubnikov-de Haas Experiments on Graphite Intercalation Compounds," M.S. Dresselhaus, G. Dresselhaus, M. Shayegan and T.C. Chieu, Proceedings of the Oji International Seminar on the Application of High Magnetic Fields in the Physics of Semiconductors and Magnetic Materials, Hakone, September, 1980, in Physics in High Magnetic Fields (ed. S. Chikazumi and N. Miura), Springer Series in Solid State Sciences 24, Springer-Verlag, New York 1981, p. 306.

6. "Low Temperature Thermal Conductivity of Graphite-$FeCl_3$ Intercalation Compounds," J. Boxus, B. Poulaert, J.P. Issi, H. Mazurek and M.S. Dresselhaus, Solid State Commun. 38, 1117 (1981).

7. "Dispersion Relations in Graphite Intercalation Compounds: Electronic Energy Bands," S.Y. Leung and G. Dresselhaus, Phys. Rev. B24, 3490 (1981).

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9. "Temperature Variation of the Thermopower of a Graphite-$FeCl_3$ Intercalation Compound," J-P. Issi, J. Boxus, B. Poulaert, H. Mazurek and M.S. Dresselhaus, J. Phys. C 14, L 307 (1981).

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11. "Neutron Scattering Experiments on Well-Staged Graphite-$FeCl_3$," J.D. Axe, C.F. Majkrzak, L. Passell, S.K. Satija, G. Dresselhaus and H. Mazurek, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 52.

12. "Scanning Transmission Electron Microscopy of Multiphases in Graphite Intercalation Compounds," H. Mazurek and M.S. Dresselhaus, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 111.

13. "Interband Landau Level Transitions in Graphite Intercalation Compounds" T.C. Chieu, M.S. Dresselhaus and G. Dresselhaus, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 68.

14. "Deformation Potential for Graphite," M.S. Dresselhaus, G. Dresselhaus and J. Heremans, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 20.

15. "Lattice Dynamics of Graphite Intercalation Compounds," S.Y. Leung, R. Al-Jishi, G. Dresselhaus and M.S. Dresselhaus, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 50.

16. "Raman Scattering Experiments on Acceptor Intercalated Graphite," A. Erbil, M. Postman, G. Dresselhaus and M. S. Dresselhaus, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 48.

17. "Magnetostriction in Graphite," J. Heremans, M. Shayegan and G. Dresselhaus, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 18.

18. "Thermal Conductivity and Thermpower Studies of Graphite Intercalation Compounds," B. Poulaert, J. Heremans, J-P. Issi, I. Zabala, H. Mazurek, and M.S. Dresselhaus, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 92.

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21. "Lattice Dynamical Model for Graphite", R. Al-Jishi, B.S. Elman and G. Dresselhaus, Fifteenth Biennial Carbon Conference, University of Pennsylvania (1981), p. 34.

22. G. Dresselhaus (invited), Bulletin of the American Physical Society 26, 264 (1981).

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24 "Magnetostriction and Deformation Potentials in Graphite", J. Heremans, J-P. Michenaud, M. Shayegan and G. Dresselhaus, J. Physics C14, 35 (1981).

25. "Low Frequency Longitudinal Lattice Modes in Graphite Intercalation Compounds", G. Dresselhaus, R. Al-Jishi, J.D., Axe, C.F. Majkrzak, L. Passell and S.K. Satija, Solid State Commun 40, 229 (1981).

26. "Effective Mass Studies of Intercalated Graphite," M.S. Dresselhaus and M. Shayegan", "Physics of Intercalation Compounds", edited by L. Pietronero and E. Tosatti, Springer, Berlin, Heidelberg, New York, 1981, Springer Series in Solid State Sciences 38, 97 (1981).

27. "Raman Scattering as a Probe of the Structural Phase Transitions in the Intercalated Graphite-Bromine System", A. Erbil, G. Dresselhaus and M.S. Dresselhaus, Phys. Rev. B25, 5451 (1982).

28. "Comparison of Transport Properties in Various Semimetals Systems", J-P. Issi, J. Heremans, G. Dresselhaus and M.S. Dresselhaus, 4th International Conference on the Physics of Narrow Gap Semiconductors, Linz, Austria, edited by E. Gornik, H. Heinrich and L. Palmetshofer, (Springer-Verlag, Berlin 1982), Lecture Notes in Physics, Vol. 152, p. 363.

29. "Shubnikov-de Haas Measurements in Alkali-Metal Graphite Intercalation Compounds", M. Shayegan, M.S. Dresselhaus and G. Dresselhaus, Physical Review B25, 4157 (1982).

30. "Phenomenological Model for Electronic Structure of Graphite Intercalation Compounds", G. Dresselhaus and S.Y. Leung, Physica 105B, 495 (1981).

31. "Magnetic Phases in Transition Metal Chloride Intercalation Compounds of Graphite", M. Elahy, C. Nicolini, G. Dresselhaus, G.O. Zimmermann, Solid State Commun. 41, 289 (1982).

32. "Scanning Transmission Electron Microscopy of Multiphases in Graphite-Alkali Metal Intercalation Compounds", H. Mazurek, M.S. Dresselhaus and G. Dresselhaus, Carbon (in press).

33. "High Magnetic Field Electronic Phase Transition in Graphite Observed by Magnetoresistance Anomaly", Y. Iye, P. Tedrow, G. Timp, M. Shayegan, M.S. Dresselhaus, G. Dresselhaus, A. Furukawa and S. Tanuma, Phys. Rev. B25, 5478 (1982).

34. "Lattice Dynamical Model for Graphite", R. Al-Jishi and G. Dresselhaus, Phys. Rev. B26 (in press).

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36. "The Effect of Intercalation on the Lattice Constants of Graphite", T. Krapchev, R. Ogilvie, and M.S. Dresselhaus, Carbon, (accepted for publication) .

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38. "Model for Raman Scattering from Incompletely Graphitized Carbons", P. Lespade, R. Al-Jishi, and M.S. Dresselhaus, Carbon (accepted for publication).

39. "Low Temperature X-ray Diffraction Study of Stage 1 Graphite-$FeCl_3$", H. Mazurek, G. Ghavamishahidi, G. Dresselhaus and M.S. Dresselhaus, Carbon accepted for publication.

40. "Intercalation Compounds", M.S. Dresselhaus, Materials Science Encyclopedia, Permagon Press Ltd. submitted.

41. "A Lattice Dynamical Model for Alkali Metal Graphite Intercalation Compounds", R. Al-Jishi and G. Dresselhaus, Phys. Rev. B26 (in press).

42. "Electron Diffraction Experiments on $C_{6n}KHg_2$", G. Dresselhaus, G. Timp, C. Nicolini, and M.S. Dresselhaus, Bulletin APS 27, 272 (1982).

43. "Optical Properties of Graphite-$CoCl_2$ Intercalation Compounds", C.W. Lowe, C. Nicolini, E. Kunoff, and G. Dresselhaus, Bulletin APS 27, 341 (1982).

44. "Magnetic Properties of Graphite Intercalation Compounds", M. Shayegan, M. Elahy, L. Salamanca-Riba, J. Heremans, C. Nicolini, and G. Dresselhaus, Bulletin APS 27, 342 (1982).

45. "High Field Magnetoconductivity of Graphite", G. Timp, Y. Iye, and G. Dresselhaus, Bulletin APS 27, 380 (1982).

46. "An Electron Microscopy Study of Stage 2 Graphite-$SbCl_5$", G. Timp and M.S. Dresselhaus, L.Salamanca-Riba and A. Erbil, L.W. Hobbs, G. Dresselhaus, P.C. Eklund, and Y. Iye, Phys. Rev. B26, 2323 (1982).

47. "Temperature Dependence of C-Axis Electrical Resistivity and Thermopower of Graphite Intercalation Compounds", J-P. Issi, B. Poulaert, J. Heremans and M.S. Dresselhaus, Solid State Commun. (accepted for publication).

48. "Observation of Superlattice-Induced Raman Modes in Graphite-Potassium-Amalgam Compounds", G. Timp, B.S. Elman, R. Al-Jishi and G. Dresselhaus, Solid State Commun. (accepted for publication).

49. "Synthesis and X-ray Characterization of Potassium-Amalgam Graphite Intercalation Compounds", Andrea B. Kress, B.S. Thesis, Physics, June, 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Under this contract a study has been carried out on the electronic, lattice, magnetic, structural, and thermal transport properties of intercalated graphite, including the modeling of these properties. The research program being carried out under this grant has been directed toward gaining an increased and fundamental understanding of the properties of graphite intercalation compounds in order to be able to produce better materials with more controlled physical properties. By using diverse experimental techniques it is possible to correlate

and interrelate the electronic, lattice, structural, magnetic and thermal transport properties of intercalated graphite and to interpret the dependence of these properties on the stage of the intercalation compound. During the two year period of this contract major advances have been made in each of these areas. Particularly noteworthy is the use of high resolution electron microscopy to monitor the c-axis and in-plane ordering on an atomic scale. Using single crystal Kish graphite host material, we have found evidence for large regions of defect-free single phase intercalant superlattices with dimensions of at least one order of magnitude greater than expected on the basis of previous work. A major advance has also been made in the use of high resolution x-ray scattering to study structural phase transitions in the graphite-bromine system which is of fundamental interest to current theoretical work on phase transitions in two-dimensions. In addition new work on superconducting compounds has been initiated.